(19) (11) Publication number: 1

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# PATENT ABSTRACTS OF JAPAN

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(71) Applicant: **SONY CORP**

(72) Inventor: **HORIE TAKESHI**
**NODA KAZUHIRO**
**YAMADA SHINICHIRO**

(74) Representative:

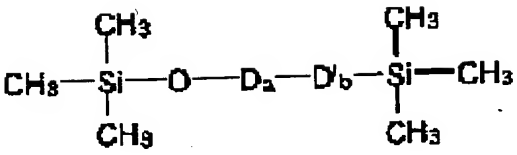
## (54) NONAQUEOUS ELECTROLYTIC SOLUTION AND NONAQUEOUS ELECTROLYTIC SOLUTION BATTERY USING THE SAME

(57) Abstract:

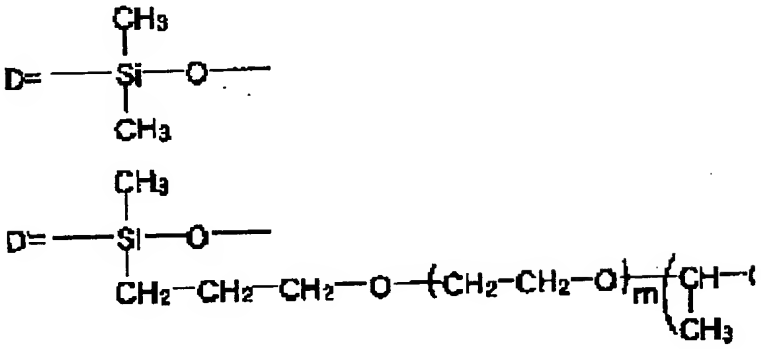
PROBLEM TO BE SOLVED: To provide a nonaqueous electrolyte solution with superior battery performance and a nonaquepous electrolytic solution battery that restrains vaporization and resolution of the electrolyte solution and simultaneously reduces the possibility of breaking and firing the battery due to a generated gas.

SOLUTION: This nonaqueous electrolyte solution battery is provided with a positive electrode, comprising an oxide or a sulfide that can be doped/dedoped with lithium ions, a negative electrode consisting of a carbon material that can be doped/dedoped with lithium metal, a

lithium alloy, or lithium ions, and a nonaqueous electrolyte solution. The nonaqueous solution is a nonaqueous solution battery comprising a siloxane derivative shown by the formula and at least one kind of lithium metallic salt. In the formula, (a) represents an integer from 1 to 50, (b) represents an integer from 1 to 20, (m) represents an integer from 0 to 40, (n) represents from 0 to 40, R represents a hydrogen element or alkyl each of which can be substituted. However, when b>1, (b) number of Ds may be the same or different.







# PATENT ABSTRACTS OF JAPAN

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(71)Applicant : SONY CORP

(72)Inventor : HORIE TAKESHI
NODA KAZUHIRO
YAMADA SHINICHIRO

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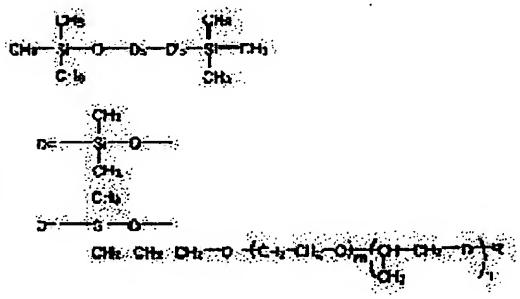

formula and at least one kind of lithium metallic salt. In the formula, (a) represents an integer from 1 to 50, (b) represents an integer from 1 to 20, (m) represents an integer from 0 to 40, (n) represents from 0 to 40, R represents a hydrogen element or alkyl each of which can be substituted. However, when b>1, (b) number of Ds may be the same or different.

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Title: **JP11214032A2: NONAQUEOUS ELECTROLYTIC SOLUTION AND NONAQUEOUS ELECTROLYTIC SOLUTION BATTERY USING THE :**

Country: **JP** Japan
Kind: **A**

Inventor: **HORIE TAKESHI;**
**NODA KAZUHIRO;**
**YAMADA SHINICHIRO;**

Assignee: **SONY CORP**
News, Profiles, Stocks and More about this company

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Abstract:

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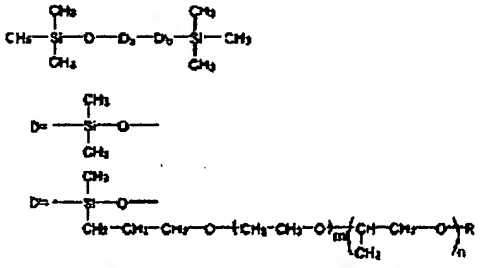
(54)【発明の名称】　非水電解液及びこれを用いた非水電解液電池

(57)【要約】

【課題】　電解液の気化、分解が抑制され、同時にガス発生による電池の破損、発火の危険性を減じ、かつ電池性能に優れる非水電解液及び非水電解液電池を提供する。

【解決手段】　リチウムイオンをドープ・脱ドープ可能な酸化物若しくは硫化物からなる正極と、リチウム金属、リチウム合金、若しくはリチウムイオンをドープ・脱ドープ可能な炭素材料からなる負極と、非水電解液を備える非水電解液電池において、当該非水電解液は、下記の化1にて示されるシロキサン誘導体と少なくとも1種のリチウム金属塩とからなる非水電解液電池。

【化1】



(式中、aは、1から50の整数を表し、bは、1から20の整数を表し、m/nは0から40の整数を表し、nは、0から40の整数を表し、Rは、水酸基またはそれぞれ置換されてもよいアルキル基を表す。ただし、b>1のときは、b個のD'は同じでも異なっていてもよい。)

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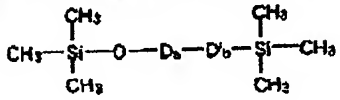
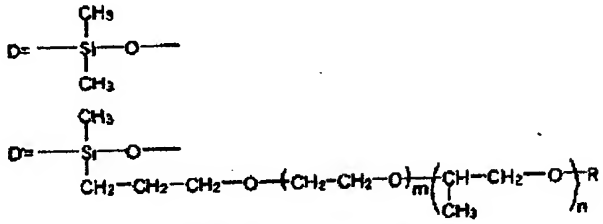
【特許請求の範囲】

【請求項１】　下記の化１にて示されるシロキサン誘導体と、少なくとも１種のアルカリ金属塩とからなることを特徴とする非水電解液。

【化１】





（式中、aは、1から50の整数を表し、bは、1から20の整数を表し、mは、0から40の整数を表し、nは、0から40の整数を表し、Rは、水素原子またはそれぞれ置換されてもよいアルキル基を表す。ただし、b>1のときは、b個のD'は同じでも異なっていてもよい。）

【請求項２】　上記シロキサン誘導体は、温度２５℃における動粘性率が５０００ｃＳｔ以下であることを特徴とする請求項１記載の非水電解液。

【請求項３】　上記シロキサン誘導体は、平均分子量が１００００以下であることを特徴とする請求項１記載の非水電解液。

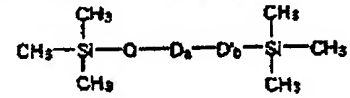
【請求項４】　上記アルカリ金属塩がリチウム金属塩であることを特徴とする請求項１記載の非水電解液。

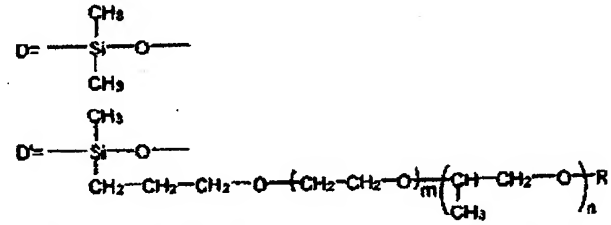
【請求項５】　温度２５℃における導電率が０．１ｍＳ・ｃｍ$^{-1}$以上であることを特徴とする請求項１記載の非※水電解液。

【請求項６】　リチウムイオンをドープ・脱ドープ可能な酸化物若しくは硫化物からなる正極と、リチウム金属、リチウム合金、若しくはリチウムイオンをドープ・脱ドープ可能な炭素材料からなる負極と、非水電解液とを備える非水電解液電池において、

上記非水電解液は、下記の化２にて示されるシロキサン誘導体と、少なくとも１種のリチウム金属塩とからなることを特徴とする非水電解液電池。

【化２】





（式中、aは、1から50の整数を表し、bは、1から20の整数を表し、mは、0から40の整数を表し、nは、0から40の整数を表し、Rは、水素原子またはそれぞれ置換されてもよいアルキル基を表す。ただし、b>1のときは、b個のD'は同じでも異なっていてもよい。）

【請求項７】　上記シロキサン誘導体は、温度２５℃における動粘性率が５０００ｃＳｔ以下であることを特徴とする請求項６記載の非水電解液電池。

【請求項８】　上記シロキサン誘導体は、平均分子量が１００００以下であることを特徴とする請求項６記載の非水電解液電池。

【請求項９】　上記非水電解液は、温度２５℃における導電率が０．１ｍＳ・ｃｍ$^{-1}$以上であることを特徴とする請求項６記載の非水電解液電池。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、特定の電解液を用いることにより、短絡時における安全性を向上させ、高電圧においても優れた電池性能を発揮する非水電解液及

びこれを用いた非水電解液電池に関するものである。

【０００２】

【従来の技術】近年になって、カメラ一体型ビデオテープレコーダ、携帯電話、ラップトップコンピュータ等の携帯用電気製品が急速に普及しつつある。また、環境保護の観点からＮＯｘ等の排気ガスを空気中に排出しない電気自動車の開発が社会的課題として取り上げられるようになった。このような状況下で、ポータブル電源、及びクリーンなエネルギー源としての電池、特に二次電池についての研究開発が活発に進められている。中でも、リチウム若しくはリチウムイオン二次電池は、従来の水系電解液二次電池である鉛電池、ニッケルカドミウム電池と比較して高いエネルギー密度が得られるため、大きな期待を集めている。

【０００３】このリチウム若しくはリチウムイオン電池の電解液としては、低分子のエチレンカーボネート、プロピレンカーボネートや、炭酸ジエチル等の炭酸エステル系非水溶媒に、電解質としてＬｉＰＦ６等のリチウム系電解質塩を溶解させた液体状態であるものが、比較的電導率も高く、電位的にも安定である点から広く用いられている。

【０００４】

【発明が解決しようとする課題】ところで、上述した非水電解液電池は、高性能であるものの、可燃性の有機溶媒を電解液として用いているため、安全性において問題がある。例えば、短絡時に急激に大電流が電池内に流れて発熱し、これによって有機溶媒を含む電解液が気化、分解をおこし、ガスを発生する問題があった。そして、＊



＊このガス発生のために、電池の破損、破裂、発火が起こる可能性があった。これまでは、これらの解決方法として、電池内圧の上昇により開裂する安全弁や電流遮断装置を設ける等の方法がなされていた。

【０００５】しかしながら、このような構造機構の改良方法では、いかなる問題にも対処できるとは限らず、電池の安全性能を向上させるには、電池材料の根本的な改善方法が必要となってきている。

【０００６】本発明は、上述のような課題を解決するために提案されたものであり、化学的、熱化学的安定性に優れた非水電解液を提供することを目的とする。そして、電解液の気化、分解を抑制し、同時にガス発生による電池の破損、発火の危険性を減じ、かつ電池性能に優れた非水電解液電池を提供することを目的とする。

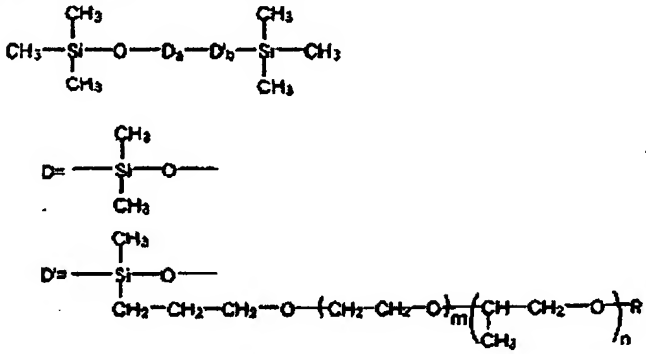
【０００７】

【課題を解決するための手段】上記目的を解決するため、本発明者らは鋭意検討を重ねた結果、電解液材料として、化学的安定性が高く、難燃性又は低蒸気圧の無機高分子であるシロキサン誘導体を用いることにより、電解液の気化、分解を抑制し、同時に電池の破損、発火の危険性を減じ、優れた電池性能を得ることができることを見いだした。

【０００８】すなわち、本発明に係る非水電解液は、下記の化３にて示されるシロキサン誘導体と、少なくとも１種のアルカリ金属塩とからなることを特徴とする。

【０００９】

【化３】



（式中、aは、1から50の整数を表し、bは、1から20の整数を表し、mは、0から40の整数を表し、nは、0から40の整数を表し、Rは、水素原子またはそれぞれ置換されてもよいアルキル基を表す。ただし、b>1のときは、b個のD'は同じでも異なっていてもよい。）

【００１０】上記シロキサン誘導体は、温度２５℃における動粘性率が５０００ｃＳｔ以下であることが好ましく、平均分子量が１００００以下であることが好ましい。動粘性率及び平均分子量が最適化されることにより、電解液として使用に耐え得る適正な粘度、混合に適する溶解性を有する溶媒の合成が可能となる。

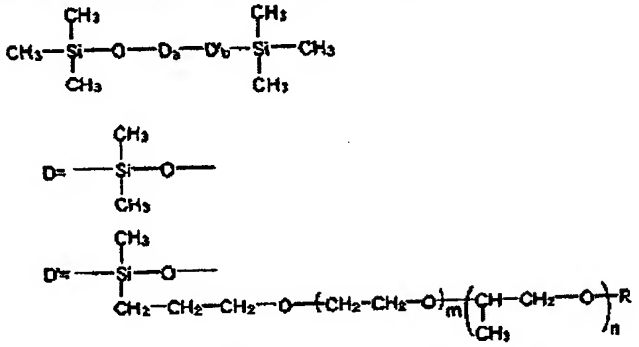
【００１１】このように、本発明に係る非水電解液は、化学安定性が高く、難燃性又は低蒸気圧の無機高分子であるシロキサン誘導体を用いていることから、短絡時においても電解液の気化、分解を抑制し、電池の破損、発火の危険性を減じ、高電圧においても優れた電池性能を有する。

【００１２】一方、本発明に係る非水電解液電池は、リチウムイオンをドープ・脱ドープ可能な酸化物若しくは

硫化物からなる正極と、リチウム金属、リチウム合金、若しくはリチウムイオンをドープ・脱ドープ可能な炭素材料からなる負極とを備える。そして、本発明に係る非水電解液電池は、下記の化４にて示されるシロキサン誘＊導体と、少なくとも１種のリチウム金属塩とからなる非水電解液を備えることを特徴とする。

【００１３】

【化４】



(式中、aは、1から50の整数を表し、bは、1から20の整数を表し、mは、0から40の整数を表し、nは、0から40の整数を表し、Rは、水素原子またはそれぞれ置換されてもよいアルキル基を表す。ただし、b>1のときは、b個のD'は同じでも異なっていてもよい。)

【００１４】上記シロキサン誘導体は、温度２５℃における動粘性率が５０００ｃＳｔ以下であることが好ましく、平均分子量が１００００以下であることが好ましい。動粘性率及び平均分子量が最適化されることにより、電解液として使用に耐え得る適正な粘度、混合に適する溶解性を有する溶媒の合成が可能となる。

【００１５】このように、本発明に係る非水電解液電池は、電解液として、化学安定性が高く、難燃性又は低蒸気圧の無機高分子であるシロキサン誘導体を用いてなることから、短絡時においても電解液の気化、分解を抑制し、電池の破損、発火の危険性を減じ、高電圧において※も優れた電池性能を有する。

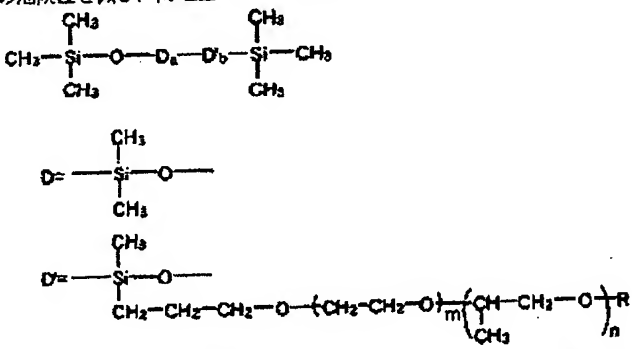
【００１６】

【発明の実施の形態】以下、本発明に係る非水電解液及びこれを用いた非水電解液電池について詳細に説明する。

【００１７】本発明に係る非水電解液は、下記の化５にて示されるシロキサン誘導体と、少なくとも１種のアルカリ金属塩とからなることを特徴とする。

【００１８】

【化５】



(式中、aは、1から50の整数を表し、bは、1から20の整数を表し、mは、0から40の整数を表し、nは、0から40の整数を表し、Rは、水素原子またはそれぞれ置換されてもよいアルキル基を表す。ただし、b>1のときは、b個のD'は同じでも異なっていてもよい。)

【００１９】上記シロキサン誘導体は、珪素と酸素の鎖状結合を基本骨格にもち、珪素に１価の有機基である側鎖基が付加された鎖状型シロキサン誘導体であり、化学的安定性が高く、難燃性若しくは低蒸気圧であるために熱化学的安定性にも優れる無機高分子である。

【００２０】さらに、このシロキサン誘導体には、粘度が比較的低い溶液状であり、かつアルカリ金属塩を溶解し得る構造が求められる。すなわち、シロキサン誘導体は、温度２５℃における動粘性率が５０００ｃＳｔ（センチストークス）以下であり、平均分子量が１００００

以下であることが求められる。

【0021】さらに、電解液としては、温度25℃における導電率が0.1mS・cm$^{-1}$以上であることがより好ましい。

【0022】電解液として使用に耐え得る適正な粘度、混合に適する溶解性は、化5で示されるD，D'の側鎖基を適度に選択することにより可能となる。化5で示されるD'の側鎖基は、エーテル結合を含むことが有利である，また、aは1～50であり、bは1～20であり．aとbの和は、1～40であることがより好ましい。なお、D．D'、及び置換基R中の水素は．フッ素．ホウ素等のハロゲン元素で置き換えられていてもよい。

【0023】一方、上述したシロキサン誘導体に溶解させるアルカリ金属塩には．リチウム．ナトリウム．アルミニウム等の軽金属の塩を使用することができ．当該非水電解液を使用する電池の種類に応じて便宜定めることができる。

【0024】例えば、リチウム若しくはリチウムイオン二次電池を構成する場合には、$LiBF_4$．$LiClO_4$、$LiPF_6$．$LiAsF_6$．$CF_3SO_3Li$、$(CF_3SO_2)_2NLi$．$C_4F_9SO_3Li$．$CF_3CO_2Li$．$(CF_3CO_2)_2NLi$、$C_4F_9SO_3Li$．$C_8F_{17}SO_3Li$、$(C_2F_5SO_2)_2NLi$、$(C_6F_5SO_2)(CF_3SO_2)NLi$、$(FSO_2C_6F_4)(CF_3SO_2)NLi$．$((CF_3)_2CHOSO_2)_2NLi$、$(CF_3SO_2)_3CLi$、$(C_3F_2(CF_3)_2-3,5)_4BLi$、$LiCF_3$．$LiAlCl_4$等のリチウム塩を使用することができる。

【0025】このように．上述したシロキサン誘導体とアルカリ金属塩を含有する非水電解液は、化学的安定性．熱化学的安定性に優れるシロキサン誘導体を溶媒として用いてなることから．短絡時に急激に大電流が流れた場合においても、電解液の気化、分解が抑制される。したがって、この非水電解液を用いた非水電解液電池は．短絡時の電池の急速な破損や発火の危険性が減じられ．安全性が向上し、かつ高電圧においても優れた電池性能を発揮することができる。

【0026】以上、上述した非水電解液は、リチウムをドープ・脱ドープ可能な酸化物若しくは硫化物からなる正極と、リチウム金属、リチウム合金．若しくはリチウムイオンをドープ・脱ドープ可能な炭素質材料からなる負極とを備えた非水電解液二次電池の電解液として用いて好適である。

【0027】例えば、リチウム二次電池を構成する場合．正極活物質としては．$TiS_2$、$MoS_2$、$NbSe_2$、$V_2O_5$等のリチウムを含有しない金属硫化物若しくは酸化物、又はリチウムを含有するリチウム複合酸化物を使用することができる。

【0028】特に、高エネルギー密度を有する電池を構成するためには．$Li_xMO_2$（式中．Mは1種類以上の遷移金属が好ましく、$0.05 \leq x \leq 1.10$である。）を主体とするリチウム複合酸化物が好ましく用いられる。リチウム複合酸化物としては．具体的に．$LiCoO_2$．$LiNiO_2$、$Li_xNi_yCo_{1-y}O_2$（式中、x．yは電池の放電状態によって異なり、通常$0<x<1.0$．$7<y\leq 1$である。）、$LiMn_2O_4$等が挙げられる。

【0029】このようなリチウム複合酸化物は．リチウムの炭酸塩、硝酸塩、酸化物、若しくは水酸化物と、コバルト、マンガン、若しくはニッケル等の炭酸塩．硝酸塩．酸化物、若しくは水酸化物とを所望の組成に応じて粉砕混合し、酸素雰囲気で600～1000℃の温度範囲で焼成することにより調整することができる。

【0030】また、負極としては、リチウム、Li－Al合金等のリチウム合金．若しくはリチウムイオンをドープ・脱ドープ可能な炭素材料等を使用することができる。炭素材料としては、所定の温度．雰囲気にて調整したものが用いられる。この原料としては、例えば．熱分解炭素類、コークス類（石油コークス．ピッチコークス等）．人造黒鉛類、天然黒鉛類、カーボンブラック（アセチレンブラック等）、ガラス状炭素類、有機高分子材料焼成体（有機高分子材料を不活性ガス気流中．あるいは真空中で500℃以上の適当な温度で焼成したもの）．炭素繊維等を使用することができる。

【0031】さらに、非水電解液の溶媒としては．上述したシロキサン誘導体の1種単独でも使用することができるが、従来公知の他の溶媒と併用して使用してもよい。他の溶媒としては、例えば、プロピレンカーボネート．エチレンカーボネート．ジエチルカーボネート、メチルエチルカーボネート．1，2－ジメトキシエタン、1．2－ジエトキシエタン．γ－ブチロラクトン．テトラヒドロフラン．1，3－ジオキソラン、ジプロピルカーボネート、ジエチルエーテル、スルホラン、メチルスルホラン、アセトニトリル．プロピルニトリル．アニソール．酢酸エステル、プロピオン酸エステル、2－メチルテトラヒドロフラン等を使用することができ．2種類以上混合して使用してもよい。

【0032】上述した正極及び負極の両極の接触による電流の短絡等を防ぐためのセパレータとしては．両極の接触を確実に防止することができ、かつ電解液を通したり含んだりすることができる材料、例えばポリテトラフルオロエチレン．ポリプロピレン、ポリエチレン等の合成樹脂製の不織布、多孔質セラミックフィルム．若しくは多孔質薄膜フィルム等を使用することができる。

【0033】このように．電解液として、化学的安定性が高く、難燃性．若しくは低蒸気圧の無機高分子のシロキサン誘導体を用いた非水電解液電池においては．電解液の気化、分解が抑制され．同時に発火、引火の危険性が減じられ、かつ高電圧においても電池性能に優れたも

のとなる。

【００３４】なお、本発明の電池のその他の構成部材としては、通常使用されているものを支障なく使用することができる。また、電池の形態は特に制限されず、コインタイプ、ボタンタイプ、ペーパータイプ、角型又はスパイラル構造の筒型電池等、電池の形態は問われない。

【００３５】

【実施例】以下、本発明を実施例により具体的に説明するが、本発明はこれに限定されるものではない。

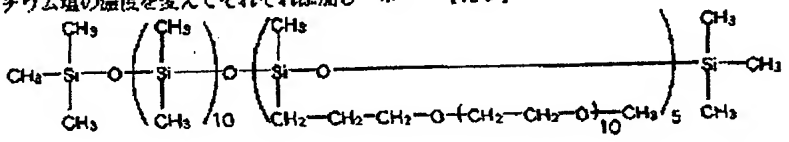
【００３６】実施例１

下記の化６～化８にて示されるシロキサン誘導体（１）～（３）にリチウム塩の濃度を変えてそれぞれ添加し＊た。そして、これらをそれぞれ厚さ０．１４５ｃｍ、面積０．７８５４ｃｍ²のステンレス板にはさみ、印加する正弦波交流電圧を記号法（複素表示）で表現した、いわゆるコール・コール（Ｃｏｌｅ－Ｃｏｌｅ）プロットから導電率を求めた。この結果を表１に示す。

【００３７】なお、各々の２５℃での粘性率は、化６で示されるシロキサン誘導体（１）が１００ｃＳｔ、化７で示されるシロキサン誘導体（２）が１６００ｃＳｔ、化８で示されるシロキサン誘導体（３）が４００ｃＳｔであった。

【００３８】

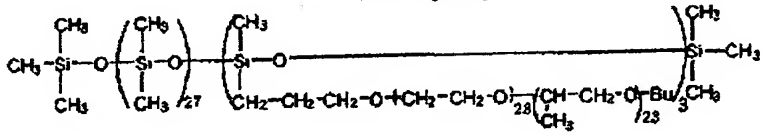
【化６】



・・・構造式（１）

【００３９】

※ ※【化７】

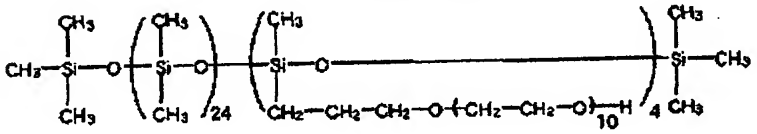


・・・構造式（２）

（Bu= ―CH₂―CH₂―CH₂―CH₃）

【００４０】

★30★【化８】



・・・構造式（３）

【００４１】

【表１】

11 12

| サンプルNo. | シロキサン誘導体 | Li塩の種類 | 電解質モル濃度(m) | 導電率(25℃)(mS・cm$^{-1}$) |
|---|---|---|---|---|
| サンプル1 | 構造式 (1) | $(CF_3SO_2)_2NLi$ | 0.5 | $2.20\times10^{-1}$ |
| サンプル2 | 構造式 (1) | $(CF_3SO_2)_2NLi$ | 1.0 | $2.25\times10^{-1}$ |
| サンプル3 | 構造式 (1) | $(CF_3SO_2)_3CLi$ | 0.5 | $1.20\times10^{-1}$ |
| サンプル4 | 構造式 (1) | $(CF_3SO_2)_3CLi$ | 1.0 | $1.26\times10^{-1}$ |
| サンプル5 | 構造式 (2) | $(CF_3SO_2)_2NLi$ | 0.5 | $2.09\times10^{-2}$ |
| サンプル6 | 構造式 (2) | $(CF_3SO_2)_2NLi$ | 1.0 | $4.05\times10^{-2}$ |
| サンプル7 | 構造式 (2) | $(CF_3SO_2)_3CLi$ | 0.5 | $3.64\times10^{-2}$ |
| サンプル8 | 構造式 (2) | $(CF_3SO_2)_3CLi$ | 1.0 | $3.80\times10^{-2}$ |
| サンプル9 | 構造式 (3) | $(CF_3SO_2)_2NLi$ | 0.5 | $4.62\times10^{-2}$ |
| サンプル10 | 構造式 (3) | $(CF_3SO_2)_2NLi$ | 1.0 | $4.80\times10^{-2}$ |
| サンプル11 | 構造式 (3) | $(CF_3SO_2)_3CLi$ | 0.5 | $2.75\times10^{-2}$ |
| サンプル12 | 構造式 (3) | $(CF_3SO_2)_3CLi$ | 1.0 | $2.88\times10^{-2}$ |

【0042】表1の結果から、化6～化8で示されるシロキサン誘導体は、いずれも電池に使用できる導電性をもつことがわかる。また、動粘性率の異なるシロキサン誘導体（1）～（3）では、より低い動粘性率を持つシロキサン誘導体（1）を用いた方がより高い導電率を得られることがわかる。

【0043】実施例2

先の化6及び化7で示されるシロキサン誘導体（1）（2）のサイクリック・ボルタモグラムを測定して酸化安定性を調べた。測定は、3電極製の電気化学セルを使用し、作用極にニッケル電極（直径：0．5mm）、対極と参照極にリチウム金属を使用した。そして、100μA・cm$^{-2}$の酸化電流が発生するまでの電位を安定な電位の範囲とした。その結果、サンプル2の酸化安定電位は、5．8V、サンプル6の酸化安定電位は、6．0Vとなった。

【0044】この結果から、シロキサン誘導体は、高電圧においても優れた電池性能を発揮できることがわかる。

＊【0045】実施例3

正極にLiCoO$_2$、負極に炭素材料、電解液に化6にて示されるシロキサン誘導体（1）用いたコインセルを作製して、充放電試験を行った。上限電圧：4．2V、下限電圧：3．0V、放電電流：100μAの条件で20サイクルまで充放電を繰り返した。その時の充放電試験を図1に示す。

【0046】図1の結果から、シロキサン誘導体（1）は、電池として優れた電池性能を有することがわかる。

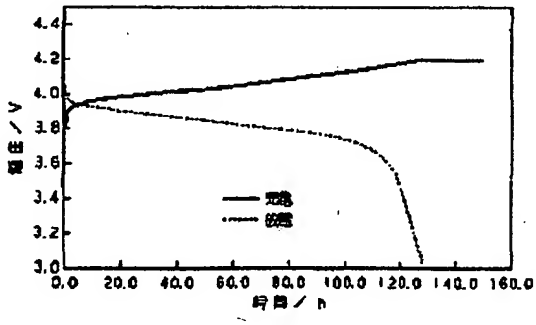
【0047】

【発明の効果】以上の説明からも明らかなように、本発明によれば、特定のシロキサン誘導体を電解液として用いてなることから、化学的、熱化学的安定性に優れた非水電解液を得ることができ、安全性に優れ、高電圧にも優れた電池性能を有する非水電解液電池を得ることができる。

【図面の簡単な説明】

【図1】本実施例の非水電解液電池の充放電曲線を示す特性図である。

【図1】




シロキサン電池の充放電曲線

* NOTICES *



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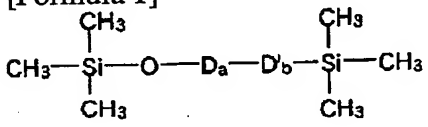
2. **** shows the word which can not be translated.
3.In the drawings, any words are not translated.

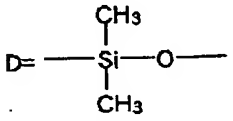
## CLAIMS

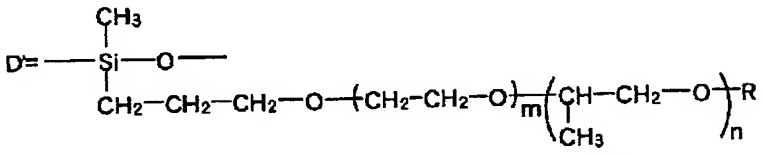
[Claim(s)]

[Claim 1] Nonaqueous electrolyte characterized by the bird clapper from the siloxane derivative shown by following ** 1, and at least one sort of alkali-metal salts.

[Formula 1]







(式中、aは、1から50の整数を表し、bは、1から20の整数を表し、mは、0から40の整数を表し、nは、0から40の整数を表し、Rは、水素原子またはそれぞれ置換されてもよいアルキル基を表す。ただし、b>1のときは、b個のD'は同じでも異なっていてもよい。)

[Claim 2] The above-mentioned siloxane derivative is nonaqueous electrolyte according to claim 1 characterized by the coefficient of kinematic viscosity in the temperature of 25 degrees C being 5000 or less cSts.

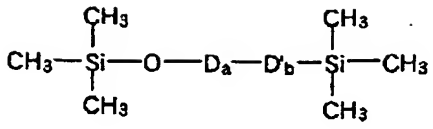
[Claim 3] The above-mentioned siloxane derivative is nonaqueous electrolyte according to claim 1 characterized by average molecular weight being 10000 or less.

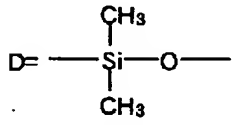
[Claim 4] Nonaqueous electrolyte according to claim 1 characterized by the above-mentioned alkali-metal salt being a lithium metal salt.

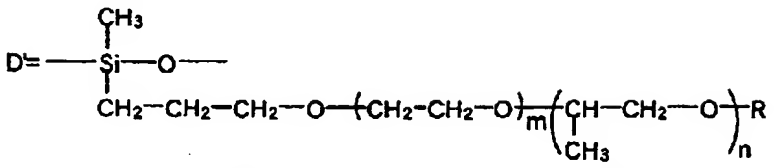
[Claim 5] Nonaqueous electrolyte according to claim 1 characterized by the conductivity in the temperature of 25 degrees C being -one or more 0.1 mS-cm.

[Claim 6] It is the nonaqueous electrolyte cell characterized by the bird clapper from the siloxane derivative in which the above-mentioned nonaqueous electrolyte is shown by following ** 2 in a nonaqueous electrolyte cell equipped with the positive electrode which consists of the oxide or sulfide in which a dope and a ** dope of a lithium ion are possible, the negative electrode which consists of a lithium metal, a lithium alloy, or a carbon material in which a dope and a ** dope of a lithium ion are possible, and nonaqueous electrolyte, and at least one sort of lithium metal salts.

[Formula 2]







(式中、aは、1から50の整数を表し、bは、1から20の整数を表し、mは、0から40の整数を表し、nは、0から40の整数を表し、Rは、水素原子またはそれぞれ置換されてもよいアルキル基を表す。ただし、b>1のときは、b個のD'は同じでも異なっていてもよい。)

[Claim 7] The above-mentioned siloxane derivative is a nonaqueous electrolyte cell according to claim 6 characterized by the coefficient of kinematic viscosity in the temperature of 25 degrees C being 5000 or less cSts.
[Claim 8] The above-mentioned siloxane derivative is a nonaqueous electrolyte cell according to claim 6 characterized by average molecular weight being 10000 or less.
[Claim 9] The above-mentioned nonaqueous electrolyte is a nonaqueous electrolyte cell according to claim 6 characterized by the conductivity in the temperature of 25 degrees C being -one or more 0.1 mS-cm.

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[Translation done.]

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## DETAILED DESCRIPTION

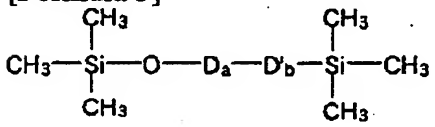
[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] By using the specific electrolytic solution, this invention raises the safety at the time of a short circuit, and relates to the nonaqueous electrolyte cell using the nonaqueous electrolyte and this which demonstrate the cell performance which was excellent also in the high voltage.
[0002]
[Description of the Prior Art] Recent years come and portable electrical-and-electric-equipment products, such as a camera one apparatus video tape recorder, a cellular phone, and a laptop computer, are spreading quickly. Moreover, development of the electric vehicle which does not discharge exhaust gas, such as NOx, in air came to be taken up from a viewpoint of environmental protection as a social technical problem. Under such a situation, the research and development about the cell as a portable power supply and a clean energy source, especially a rechargeable battery are furthered actively. Especially, since a high energy density is obtained as compared with the lead cell and nickel-cadmium battery which are the conventional drainage system electrolytic-solution rechargeable battery, the lithium or the rechargeable lithium-ion battery attracts great expectation.
[0003] As the electrolytic solution of this lithium or a lithium ion battery, also as for electric conductivity, what is in the liquid state where the lithium system electrolyte salt of LiPF6 grade was dissolved as an electrolyte is comparatively high to low-molecular ethylene carbonate, propylene carbonate, and carbonate system non-aqueous solvents, such as diethyl carbonate, and is widely used for them from the point stable also in potential.
[0004]
[Problem(s) to be Solved by the Invention] By the way, although the nonaqueous electrolyte cell mentioned above is highly efficient, since the inflammable organic solvent is used for it as the electrolytic solution, it has a problem in safety. For example, the high current flowed and generated heat in the cell rapidly at the time of a short circuit, the electrolytic solution which contains an organic solvent by this caused evaporation and decomposition, and there was a problem which generates gas. And breakage of a cell, rupture, and ignition may have taken place for this generation of gas. Methods, such as preparing the relief valve and current interrupting device which cleave by elevation of cell internal pressure as these solution methods until now, were made.
[0005] However, by such improvement method of a structure mechanism, in order not to restrict that any problems can be coped with but to raise the safe performance of a cell, the fundamental improvement method of cell material is needed.
[0006] this invention is proposed in order to solve the above technical problems, and it aims at offering nonaqueous electrolyte excellent in chemical and thermochemical stability. And it aims at offering the nonaqueous electrolyte cell which suppressed evaporation of the electrolytic solution, and decomposition, and reduced breakage of the cell by the generation of gas, and the danger of ignition simultaneously, and was excellent in the cell performance.
[0007]
[Means for Solving the Problem] In order to solve the above-mentioned purpose, this invention persons had high chemical stability as an electrolytic-solution material, as a result of repeating examination wholeheartedly, and by using the siloxane derivative which is the inorganic polymer of

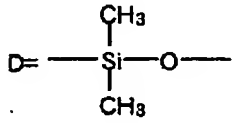
fire-resistant or low vapor pressure, evaporation of the electrolytic solution and decomposition were suppressed, breakage of a cell and the danger of ignition were reduced simultaneously, and it found out that the outstanding cell performance could be obtained.

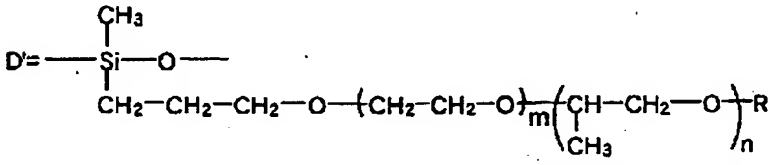
[0008] That is, the nonaqueous electrolyte concerning this invention is characterized by the bird clapper from the siloxane derivative shown by following ** 3, and at least one sort of alkali-metal salts.

[0009]

[Formula 3]







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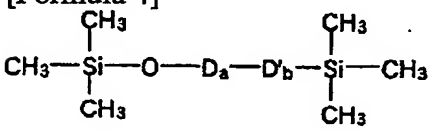
[0010] As for the above-mentioned siloxane derivative, it is desirable that the coefficient of kinematic viscosity in the temperature of 25 degrees C is 5000 or less cSts, and it is desirable that average molecular weight is 10000 or less. By optimizing a coefficient of kinematic viscosity and average molecular weight, it becomes compoundable [ the solvent which has the proper viscosity which can be equal to use as the electrolytic solution, and the solubility suitable for mixture ].

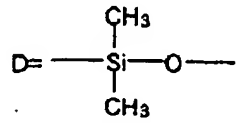
[0011] Thus, the nonaqueous electrolyte concerning this invention has high chemistry stability, since the siloxane derivative which is the inorganic polymer of fire-resistant or low vapor pressure is used for it, it suppresses evaporation of the electrolytic solution, and decomposition at the time of a short circuit, reduces breakage of a cell, and the danger of ignition, and has the cell performance which was excellent also in the high voltage.

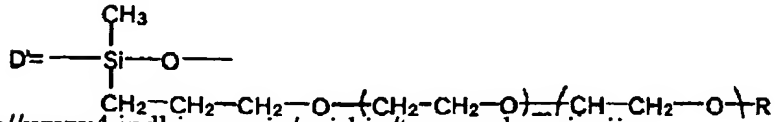
[0012] On the other hand, the nonaqueous electrolyte cell concerning this invention is equipped with the positive electrode which consists of the oxide or sulfide in which a dope and a ** dope of a lithium ion are possible, and the negative electrode which consists of a lithium metal, a lithium alloy, or a carbon material in which a dope and a ** dope of a lithium ion are possible. And the nonaqueous electrolyte cell concerning this invention is characterized by having nonaqueous electrolyte which consists of a siloxane derivative shown by following ** 4, and at least one sort of lithium metal salts.

[0013]

[Formula 4]







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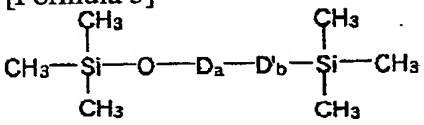
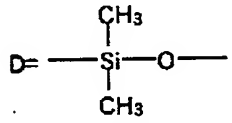
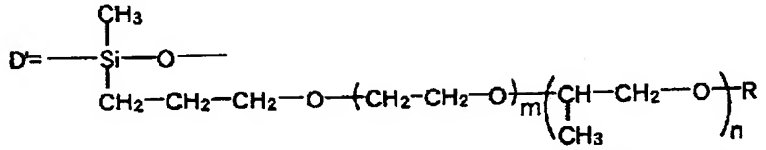
[0014] As for the above-mentioned siloxane derivative, it is desirable that the coefficient of kinematic viscosity in the temperature of 25 degrees C is 5000 or less cSts, and it is desirable that average molecular weight is 10000 or less. By optimizing a coefficient of kinematic viscosity and average molecular weight, it becomes compoundable [ the solvent which has the proper viscosity which can be equal to use as the electrolytic solution, and the solubility suitable for mixture ].
[0015] Thus, as the electrolytic solution, the nonaqueous electrolyte cell concerning this invention has high chemistry stability, using the siloxane derivative which is the inorganic polymer of fire-resistant or low vapor pressure, it suppresses evaporation of the electrolytic solution, and decomposition at the time of a short circuit, reduces breakage of a cell, and the danger of ignition, and has the cell performance which was excellent also in the high voltage from a bird clapper.
[0016]
[Embodiments of the Invention] Hereafter, the nonaqueous electrolyte cell using the nonaqueous electrolyte and this concerning this invention is explained in detail.
[0017] The nonaqueous electrolyte concerning this invention is characterized by the bird clapper from the siloxane derivative shown by following ** 5, and at least one sort of alkali-metal salts.
[0018]
[Formula 5]







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[0019] It is the shape type siloxane derivative of a chain with which it had the chain combination of a silicon and oxygen in the basic skeleton, and the side chain radical which is a univalent organic machine was added to the silicon, its chemical stability is high, and since the above-mentioned siloxane derivative is fire retardancy or low vapor pressure, it is an inorganic polymer which is excellent also in thermochemical stability.
[0020] Furthermore, viscosity is a low solution-like comparatively, and this siloxane derivative is asked for the structure where an alkali-metal salt may be dissolved. That is, coefficients of kinematic viscosity [ in / the temperature of 25 degrees C / in a siloxane derivative ] are below 5000cSt(s) (centistokes), and it is called for that average molecular weight is 10000 or less.
[0021] Furthermore, it is more desirable that the conductivity in the temperature of 25 degrees C is - one or more 0.1 mS-cm as the electrolytic solution.
[0022] The proper viscosity which can be equal to use as the electrolytic solution, and the solubility suitable for mixture become possible by choosing moderately the side chain radical of D shown by **

5, and D'. As for the side chain radical of D' shown by ** 5, it is advantageous to include ether linkage. Moreover, a is 1-50, b is 1-20 and, as for the sum of a and b, it is more desirable that it is 1-40. In addition, the hydrogen in D, D', and Substituent R may be replaced by halogens, such as a fluorine and boron.

[0023] According to the kind of cell which can use the salt of light metals, such as a lithium, sodium, and aluminum, and uses the nonaqueous electrolyte concerned, it can set to the alkali-metal salt dissolved in the siloxane derivative mentioned above on the other hand expedient.

[0024] for example, in constituting a lithium or a rechargeable lithium-ion battery LiBF4, LiClO4, LiPF6, LiAsF6, CF3SO3Li, 2NLi, C4F9SO3Li, CF3CO2Li, (CF3SO2) 2NLi, C6F5SO3Li, C8F17SO3Li, (CF3CO2) It NLi(s) and NLi(s) (CF(C4F9SO2)3SO2). (C2F5SO2) 2 -- (FSO2C6F4) NLi, 2(2(CF3) CHOSO2) NLi, 3(CF3SO2) CLi, and 4 (3 C6F3(CF3)2- 5) -- the lithium salt of BLi, LiCF3, and LiAlCl4 grade can be used (CF3SO2)

[0025] Thus, when a high current flows rapidly from a bird clapper at the time of a short circuit, using as a solvent the siloxane derivative the nonaqueous electrolyte containing the siloxane derivative mentioned above and an alkali-metal salt excels [ derivative ] in chemical stability and thermochemical stability, evaporation of the electrolytic solution and decomposition are suppressed. Therefore, the cell performance which the danger of rapid breakage of the cell at the time of a short circuit or ignition was reduced, and safety of the nonaqueous electrolyte cell using this nonaqueous electrolyte improved, and was excellent also in the high voltage can be demonstrated.

[0026] As mentioned above, the nonaqueous electrolyte mentioned above uses as the electrolytic solution of the nonaqueous electrolyte rechargeable battery equipped with the positive electrode which consists of the oxide or sulfide in which a dope and a ** dope of a lithium are possible, and the negative electrode which consists of carbonaceous material in which a dope and a ** dope of a lithium metal, a lithium alloy, or a lithium ion are possible and is suitable.

[0027] For example, when it constitutes a lithium secondary battery, as a positive active material, the metallic sulfide which does not contain the lithium of TiS2, MoS2, NbSe2, and V2O5 grade, an oxide, or the lithium multiple oxide containing a lithium can be used.

[0028] In order to constitute the cell which has high-energy density especially, the lithium multiple oxide which makes a subject LixMO2 (one or more kinds of transition metals of M are desirable, and it is 0.05<=x<=1.10 among a formula.) is used preferably. As a lithium multiple oxide, LiCoO2, LiNiO2, LixNiyCo1-yO2 (among a formula, x and y change with electric discharge states of a cell, and are usually 0< x<1 and 0.7< y<=1.), and LiMn2O4 grade are mentioned concretely.

[0029] According to composition of a request of the carbonate of a lithium, a nitrate, an oxide or a hydroxide, and carbonates, such as cobalt, manganese, or nickel, a nitrate, an oxide or a hydroxide, trituration mixture of such a lithium multiple oxide can be carried out, and it can be adjusted by calcinating by the 600-1000-degree C temperature requirement in oxygen atmosphere.

[0030] Moreover, as a negative electrode, lithium alloys, such as a lithium and an Li-aluminum alloy, or the carbon material in which a dope and a ** dope of a lithium ion are possible can be used. What was adjusted in predetermined temperature and atmosphere as a carbon material is used. As this raw material, pyrolytic carbons, corks, artificial graphites (petroleum coke, pitch coke, etc.), natural graphites, carbon black (acetylene black etc.), glassy carbons, an organic polymeric-materials baking object (what calcinated organic polymeric materials at the suitable temperature of 500 degrees C or more in the inert gas air current or the vacuum), a carbon fiber, etc. can be used, for example.

[0031] Furthermore, although it can use the one-sort independent which is the siloxane derivative mentioned above as a solvent of nonaqueous electrolyte, you may use it conventionally, using together with other well-known solvents. As other solvents, propylene carbonate, ethylene carbonate, diethyl carbonate, methylethyl carbonate, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, gamma-butyrolactone, a tetrahydrofuran, 1, 3-dioxolane, dipropyl carbonate, diethylether, a sulfolane, a methyl sulfolane, an acetonitrile, propyl nitril, an anisole, acetic ester, propionic-acid ester, 2-methyl tetrahydrofuran, etc. can be used, and two or more kinds may use it, for example, mixing.

[0032] A nonwoven fabric, a porosity ceramic film, or a porosity thin film film made of synthetic resin, such as the material which can prevent contact of two poles certainly, and, and can contain or can be carried out as separator for preventing the short circuit of the current by contact of the positive

electrode mentioned above and the two poles of a negative electrode etc., for example, a polytetrafluoroethylene, polypropylene, and polyethylene, etc. can be used. [ letting the electrolytic solution pass ]

[0033] Thus, as the electrolytic solution, chemical stability is high and it becomes what evaporation of the electrolytic solution and decomposition were suppressed, and the danger of ignition and ignition was simultaneously reduced, and was excellent in the cell performance also in the high voltage in the nonaqueous electrolyte cell using the siloxane derivative of the inorganic polymer of fire-resistant or low vapor pressure.

[0034] In addition, as a composition member of others of the cell of this invention, what is usually used can be used convenient. Moreover, especially the gestalt of a cell is not restricted and the gestalt of cells, such as a telescopic cell of a coin type, a button type, a paper type, a square shape, or spiral structure, is not asked.

[0035]

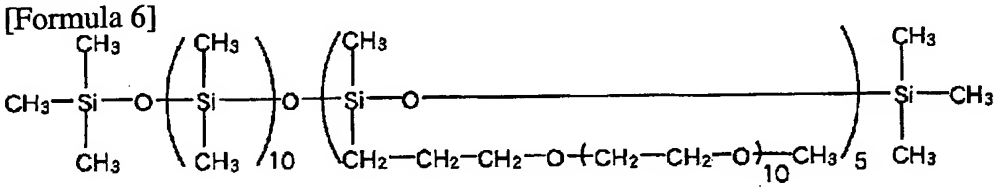
[Example] Hereafter, although an example explains this invention concretely, this invention is not limited to this.

[0036] The concentration of lithium salt was changed into siloxane derivative (1) - (3) shown by ** 6 of the example 1 following --izing 8, and it added, respectively. And these were inserted into the stainless steel board of 2 the thickness of 0.145cm, and an area of 0.7854cm, respectively, and it asked for conductivity from the so-called Kohl Kohl (Cole-Cole) plot which expressed the sine-wave-alternating-current voltage to impress by the symbolic method (complex notation). This result is shown in Table 1.

[0037] In addition, the siloxane derivatives (3) in which the siloxane derivative (2) in which the siloxane derivative (1) in which the coefficient of kinematic viscosity in each 25 degrees C is shown by ** 6 is shown by 100cSt(s) and ** 7 is shown by 1600cSt(s) and ** 8 were 400cSt(s).

[0038]

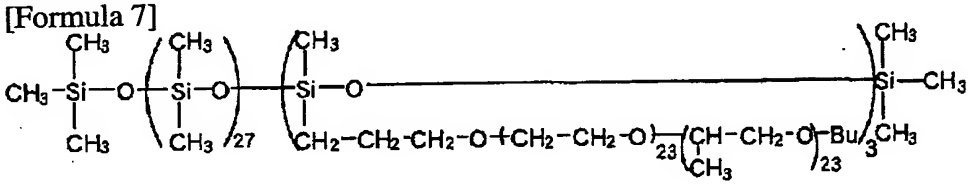
[Formula 6]



・・・構造式（1）

[0039]

[Formula 7]

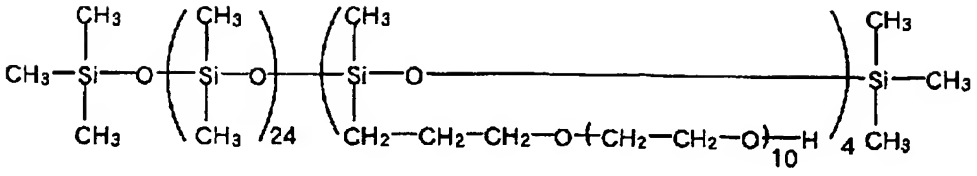


・・・構造式（2）

(Bu= ——$CH_2$—$CH_2$—$CH_2$—$CH_3$)

[0040]

[Formula 8]



・・・構造式（3）

[0041]
[Table 1]

| サンプルNo. | シロキサン誘導体 | Li塩の種類 | 重量モル濃度(m) | 導電率(25℃)[mS・cm$^{-1}$] |
|---|---|---|---|---|
| サンプル1 | 構造式（1） | $(CF_3SO_2)_2NLi$ | 0.5 | $2.20\times10^{-1}$ |
| サンプル2 | 構造式（1） | $(CF_3SO_2)_2NLI$ | 1.0 | $2.25\times10^{-1}$ |
| サンプル3 | 構造式（1） | $(CF_3SO_2)_3CLi$ | 0.5 | $1.20\times10^{-1}$ |
| サンプル4 | 構造式（1） | $(CF_3SO_2)_3CLi$ | 1.0 | $1.26\times10^{-1}$ |
| サンプル5 | 構造式（2） | $(CF_3SO_2)_2NLi$ | 0.5 | $2.09\times10^{-2}$ |
| サンプル6 | 構造式（2） | $(CF_3SO_2)_2NLi$ | 1.0 | $4.05\times10^{-2}$ |
| サンプル7 | 構造式（2） | $(CF_3SO_2)_3CLI$ | 0.5 | $3.64\times10^{-2}$ |
| サンプル8 | 構造式（2） | $(CF_3SO_2)_3CLI$ | 1.0 | $3.80\times10^{-2}$ |
| サンプル9 | 構造式（3） | $(CF_3SO_2)_2NLi$ | 0.5 | $4.62\times10^{-2}$ |
| サンプル10 | 構造式（3） | $(CF_3SO_2)_2NLi$ | 1.0 | $4.80\times10^{-2}$ |
| サンプル11 | 構造式（3） | $(CF_3SO_2)_3CLi$ | 0.5 | $2.75\times10^{-2}$ |
| サンプル12 | 構造式（3） | $(CF_3SO_2)_3CLI$ | 1.0 | $2.88\times10^{-2}$ |

[0042] The result of Table 1 shows that each siloxane derivative shown by ** 6 --izing 8 has the conductivity which can be used for a cell. Moreover, in siloxane derivative (1) - (3) from which a coefficient of kinematic viscosity differs, it turns out that conductivity with higher using the siloxane derivative (1) which has a low coefficient of kinematic viscosity more can be obtained.
[0043] The cyclic voltamogram of the siloxane derivative (1) shown by ** 6 and ** 7 of the example 2 point and (2) was measured, and oxidation stability was investigated. Measurement used the electrochemical cell made from three electrodes, and used the lithium metal for the operation pole on the nickel electrode (diameter : 0.5mm), the counter electrode, and the reference pole. And potential until the oxidation current of 100microA-cm -2 occurs was made into the range of stable potential. Consequently, 5.8V and the oxidization stable potential of a sample 6 were set to 6.0V by the oxidization stable potential of a sample 2.
[0044] This result shows that a siloxane derivative can demonstrate the cell performance which was excellent also in the high voltage.
[0045] The coin cell siloxane derivative [ which is shown to LiCoO2 and a negative electrode by the carbon material, and is shown in the electrolytic solution by ** 6 ] (1) Used for example 3 positive electrode was produced, and the charge and discharge test was performed. Upper-limit voltage: Charge and discharge were repeated up to 20 cycles on condition that 4.2V, minimum voltage:3.0V, and discharge current:100microA. The charge and discharge test at that time is shown in drawing 1 .
[0046] The result of drawing 1 shows that a siloxane derivative (1) has the cell performance which was excellent as a cell.
[0047]
[Effect of the Invention] According to this invention, the nonaqueous electrolyte cell which has the cell performance which could obtain nonaqueous electrolyte excellent in chemical and thermochemical stability, was excellent in safety, and was excellent also in the high voltage from the bird clapper can be obtained, using a specific siloxane derivative as the electrolytic solution so that clearly also from the above explanation.

[Translation done.]

* NOTICES *



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2. **** shows the word which can not be translated.
3.In the drawings, any words are not translated.

## TECHNICAL FIELD

[The technical field to which invention belongs] By using the specific electrolytic solution, this invention raises the safety at the time of a short circuit, and relates to the nonaqueous electrolyte cell using the nonaqueous electrolyte and this which demonstrate the cell performance which was excellent also in the high voltage.

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PRIOR ART

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[Description of the Prior Art] Recent years come and portable electrical-and-electric-equipment products, such as a camera one apparatus video tape recorder, a cellular phone, and a laptop computer, are spreading quickly. Moreover, development of the electric vehicle which does not discharge exhaust gas, such as NOx, in air came to be taken up from a viewpoint of environmental protection as a social technical problem. Under such a situation, the research and development about the cell as a portable power supply and a clean energy source, especially a rechargeable battery are furthered actively. Especially, since a high energy density is obtained as compared with the lead cell and nickel-cadmium battery which are the conventional drainage system electrolytic-solution rechargeable battery, the lithium or the rechargeable lithium-ion battery attracts great expectation.
[0003] As the electrolytic solution of this lithium or a lithium ion battery, also as for electric conductivity, what is in the liquid state where the lithium system electrolyte salt of LiPF6 grade was dissolved as an electrolyte is comparatively high to low-molecular ethylene carbonate, propylene carbonate, and carbonate system non-aqueous solvents, such as diethyl carbonate, and is widely used for them from the point stable also in potential.

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## EFFECT OF THE INVENTION

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## TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] By the way, although the nonaqueous electrolyte cell mentioned above is highly efficient, since the inflammable organic solvent is used for it as the electrolytic solution, it has a problem in safety. For example, the high current flowed and generated heat in the cell rapidly at the time of a short circuit, the electrolytic solution which contains an organic solvent by this caused evaporation and decomposition, and there was a problem which generates gas. And breakage of a cell, a burst, and ignition may have taken place for this generation of gas. Methods, such as preparing the relief valve and current interrupting device which cleave by the rise of cell internal pressure as these solution methods until now, were made.

[0005] However, by such improvement method of a structure mechanism, in order not to restrict that any problems can be coped with but to raise the safe performance of a cell, the fundamental improvement method of cell material is needed.

[0006] this invention is proposed in order to solve the above technical problems, and it aims at offering nonaqueous electrolyte excellent in chemical and thermochemical stability. And it aims at offering the nonaqueous electrolyte cell which suppressed evaporation of the electrolytic solution, and decomposition, and reduced breakage of the cell by the generation of gas, and the danger of ignition simultaneously, and was excellent in the cell performance.

[Translation done.]

* NOTICES *



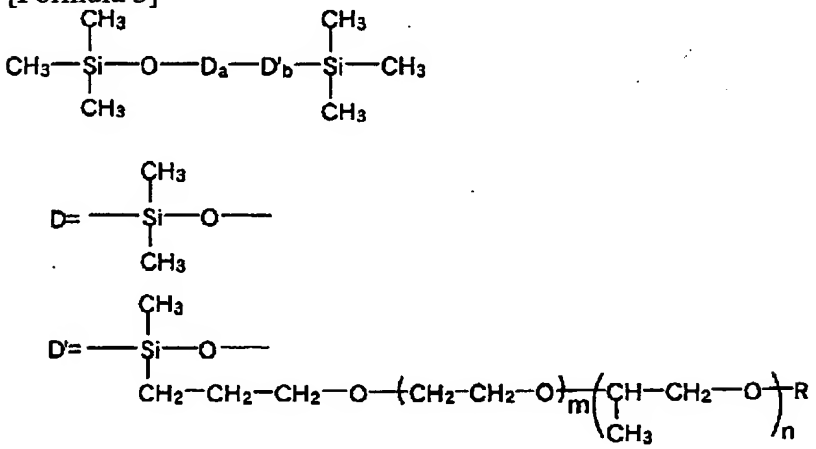
## MEANS

[Means for Solving the Problem] In order to solve the above-mentioned purpose, this invention persons had high chemical stability as an electrolytic-solution material, as a result of repeating examination wholeheartedly, and by using the siloxane derivative which is the inorganic polymer of fire-resistant or low vapor pressure, evaporation of the electrolytic solution and decomposition were suppressed, breakage of a cell and the danger of ignition were reduced simultaneously, and it found out that the outstanding cell performance could be obtained.

[0008] That is, the nonaqueous electrolyte concerning this invention is characterized by the bird clapper from the siloxane derivative shown by following ** 3, and at least one sort of alkali-metal salts.

[0009]

[Formula 3]



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[0010] As for the above-mentioned siloxane derivative, it is desirable that the coefficient of kinematic viscosity in the temperature of 25 degrees C is 5000 or less cSts, and it is desirable that average molecular weight is 10000 or less. By optimizing a coefficient of kinematic viscosity and average molecular weight, it becomes compoundable [ the solvent which has the proper viscosity which can be equal to use as the electrolytic solution, and the solubility suitable for mixture ].

[0011] Thus, the nonaqueous electrolyte concerning this invention has high chemistry stability, since the siloxane derivative which is the inorganic polymer of fire-resistant or low vapor pressure is used for it, it suppresses evaporation of the electrolytic solution, and decomposition at the time of a short circuit, reduces breakage of a cell, and the danger of ignition, and has the cell performance which was excellent also in the high voltage.

[0012] On the other hand, the nonaqueous electrolyte cell concerning this invention is equipped with the positive electrode which consists of the oxide or sulfide in which a dope and a ** dope of a lithium ion are possible, and the negative electrode which consists of a lithium metal, a lithium alloy, or a carbon material in which a dope and a ** dope of a lithium ion are possible. And the nonaqueous

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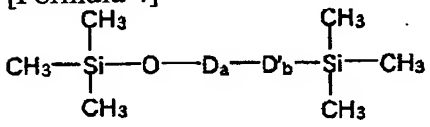
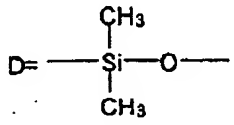
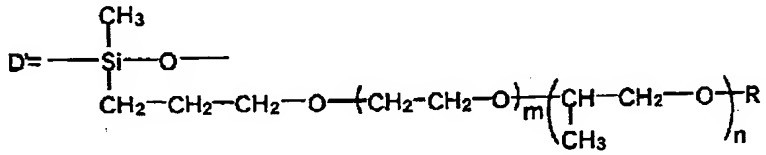
[0013]

[Formula 4]







(式中、aは、1から50の整数を表し、bは、1から20の整数を表し、mは、0から40の整数を表し、nは、0から40の整数を表し、Rは、水素原子またはそれぞれ置換されてもよいアルキル基を表す。ただし、b>1のときは、b個のD'は同じでも異なっていてもよい。)

[0014] As for the above-mentioned siloxane derivative, it is desirable that the coefficient of kinematic viscosity in the temperature of 25 degrees C is 5000 or less cSts, and it is desirable that average molecular weight is 10000 or less. By optimizing a coefficient of kinematic viscosity and average molecular weight, it becomes compoundable [ the solvent which has the proper viscosity which can be equal to use as the electrolytic solution, and the solubility suitable for mixture ].

[0015] Thus, as the electrolytic solution, the nonaqueous electrolyte cell concerning this invention has high chemistry stability, using the siloxane derivative which is the inorganic polymer of fire-resistant or low vapor pressure, it suppresses evaporation of the electrolytic solution, and decomposition at the time of a short circuit, reduces breakage of a cell, and the danger of ignition, and has the cell performance which was excellent also in the high voltage from a bird clapper.

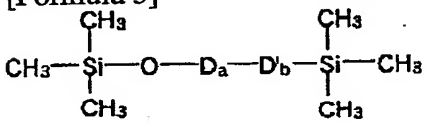
[0016]

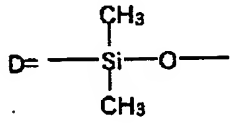
[Embodiments of the Invention] Hereafter, the nonaqueous electrolyte cell using the nonaqueous electrolyte and this concerning this invention is explained in detail.

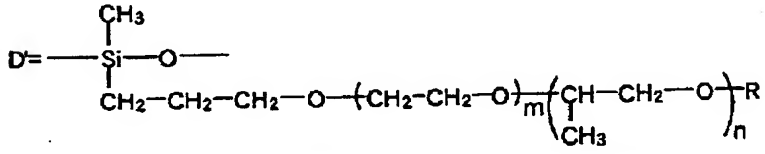
[0017] The nonaqueous electrolyte concerning this invention is characterized by the bird clapper from the siloxane derivative shown by following ** 5, and at least one sort of alkali-metal salts.

[0018]

[Formula 5]







(式中、aは、1から50の整数を表し、bは、1から20の整数を表し、mは、0から40の整数を表し、nは、0から40の整数を表し、Rは、水素原子またはそれぞれ置換されてもよいアルキル基を表す。ただし、b>1のときは、b個のD'は同じでも異なっていてもよい。)

[0019] It is the shape type siloxane derivative of a chain with which it had the chain combination of a silicon and oxygen in the basic frame, and the side chain radical which is a univalent organic machine was added to the silicon, its chemical stability is high, and since the above-mentioned siloxane derivative is fire retardancy or low vapor pressure, it is an inorganic polymer which is excellent also in thermochemical stability.
[0020] Furthermore, the structure where it has the shape of a solution with comparatively low viscosity, and an alkali-metal salt may be dissolved in this siloxane derivative is searched for. That is, coefficients of kinematic viscosity [ in / the temperature of 25 degrees C / in a siloxane derivative ] are below 5000cSt(s) (centistokes), and it is called for that average molecular weight is 10000 or less.

[0021] Furthermore, it is more desirable that the conductivity in the temperature of 25 degrees C is - one or more 0.1 mS-cm as the electrolytic solution.
[0022] The proper viscosity which can be equal to use as the electrolytic solution, and the solubility suitable for mixture become possible by choosing moderately the side chain radical of D shown by ** 5, and D'. As for the side chain radical of D' shown by ** 5, it is advantageous to include ether linkage. Moreover, a is 1-50, b is 1-20 and, as for the sum of a and b, it is more desirable that it is 1-40. In addition, the hydrogen in D, D', and Substituent R may be replaced by halogens, such as a fluorine and boron.
[0023] According to the kind of cell which can use the salt of light metals, such as a lithium, sodium, and aluminum, and uses the nonaqueous electrolyte concerned, it can set to the alkali-metal salt dissolved in the siloxane derivative mentioned above on the other hand expedient.
[0024] for example, in constituting a lithium or a rechargeable lithium-ion battery LiBF4, LiClO4, LiPF6, LiAsF6, CF3SO3Li, 2NLi, C4F9SO3Li, CF3CO2Li, (CF3SO2) 2NLi, C6F5SO3Li, C8F17SO3Li, (CF3CO2) It NLi(s) and NLi(s) (CF(C4F9SO2)3SO2). (C2F5SO2) 2 -- (FSO2C6F4) NLi, 2(2(CF3) CHOSO2) NLi, 3(CF3SO2) CLi, and 4 (3 C6F3(CF3)2- 5) -- the lithium salt of BLi, LiCF3, and LiAlCl4 grade can be used (CF3SO2)
[0025] Thus, when a high current flows rapidly from a bird clapper at the time of a short circuit, using as a solvent the siloxane derivative the nonaqueous electrolyte containing the siloxane derivative mentioned above and an alkali-metal salt excels [ derivative ] in chemical stability and thermochemical stability, evaporation of the electrolytic solution and decomposition are suppressed. Therefore, the cell performance which the danger of rapid breakage of the cell at the time of a short circuit or ignition was reduced, and safety of the nonaqueous electrolyte cell using this nonaqueous electrolyte improved, and was excellent also in the high voltage can be demonstrated.
[0026] As mentioned above, the nonaqueous electrolyte mentioned above uses as the electrolytic solution of the nonaqueous electrolyte rechargeable battery equipped with the positive electrode which consists of the oxide or sulfide in which a dope and a ** dope of a lithium are possible, and the negative electrode which consists of carbonaceous material in which a dope and a ** dope of a lithium metal, a lithium alloy, or a lithium ion are possible and is suitable.
[0027] For example, when it constitutes a lithium secondary battery, as a positive active material, the metallic sulfide which does not contain the lithium of TiS2, MoS2, NbSe2, and V2O5 grade, an oxide, or the lithium multiple oxide containing a lithium can be used.
[0028] In order to constitute the cell which has high-energy density especially, the lithium multiple oxide which makes a subject LixMO2 (one or more kinds of transition metals of M are desirable, and it is 0.05<=x<=1.10 among a formula.) is used preferably. As a lithium multiple oxide, LiCoO2, LiNiO2, LixNiyCo1-yO2 (among a formula, x and y change with electric discharge states of a cell, and are usually 0< x<1 and 0.7< y<=1.), and LiMn2O4 grade are mentioned concretely.
[0029] According to composition of a request of the carbonate of a lithium, a nitrate, an oxide or a hydroxide, and carbonates, such as cobalt, manganese, or nickel, a nitrate, an oxide or a hydroxide, pulverization mixture of such a lithium multiple oxide can be carried out, and it can be adjusted by calcinating by the 600-1000-degree C temperature requirement in oxygen atmosphere.
[0030] Moreover, as a negative electrode, lithium alloys, such as a lithium and an Li-aluminum alloy, or the carbon material in which a dope and a ** dope of a lithium ion are possible can be used. What

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## EXAMPLE

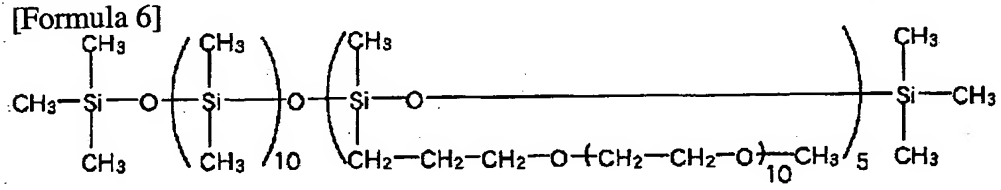
[Example] Hereafter, although an example explains this invention concretely, this invention is not limited to this.

[0036] The concentration of lithium salt was changed into siloxane derivative (1) - (3) shown by ** 6 of the example 1 following --izing 8, and it added, respectively. And these were inserted into the stainless steel board of 2 the thickness of 0.145cm, and an area of 0.7854cm, respectively, and it asked for conductivity from the so-called Kohl Kohl (Cole-Cole) plot which expressed the sine-wave-alternating-current voltage to impress by the symbolic method (complex notation). This result is shown in Table 1.

[0037] In addition, the siloxane derivatives (3) in which the siloxane derivative (2) in which the siloxane derivative (1) in which the coefficient of kinematic viscosity in each 25 degrees C is shown by ** 6 is shown by 100cSt(s) and ** 7 is shown by 1600cSt(s) and ** 8 were 400cSt(s).

[0038]

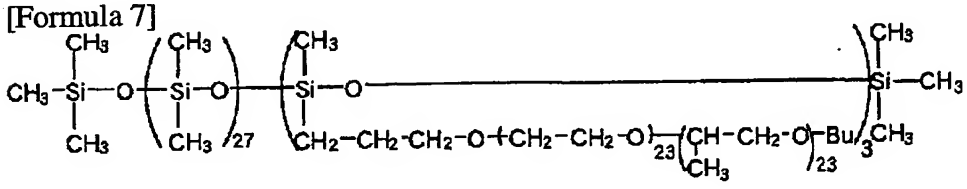
[Formula 6]



・・・構造式（1）

[0039]

[Formula 7]

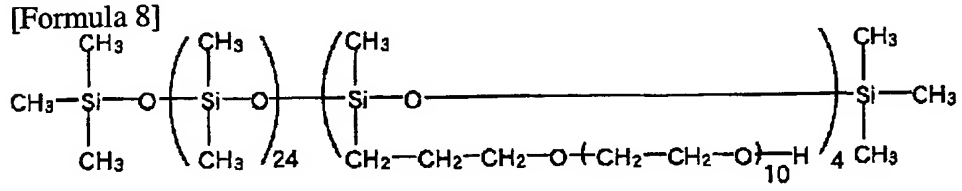


・・・構造式（2）

（Bu= ——$CH_2$—$CH_2$—$CH_2$—$CH_3$）

[0040]

[Formula 8]



・・・構造式（3）

[0041]
[Table 1]

| サンプルNo. | シロキサン誘導体 | Li塩の種類 | 重量モル濃度(m) | 導電率(25℃)[mS・cm$^{-1}$] |
|---|---|---|---|---|
| サンプル1 | 構造式 (1) | $(CF_3SO_2)_2NLi$ | 0.5 | $2.20\times10^{-1}$ |
| サンプル2 | 構造式 (1) | $(CF_3SO_2)_2NLI$ | 1.0 | $2.25\times10^{-1}$ |
| サンプル3 | 構造式 (1) | $(CF_3SO_2)_3CLi$ | 0.5 | $1.20\times10^{-1}$ |
| サンプル4 | 構造式 (1) | $(CF_3SO_2)_3CLi$ | 1.0 | $1.26\times10^{-1}$ |
| サンプル5 | 構造式 (2) | $(CF_3SO_2)_2NLi$ | 0.5 | $2.09\times10^{-2}$ |
| サンプル6 | 構造式 (2) | $(CF_3SO_2)_2NLi$ | 1.0 | $4.05\times10^{-2}$ |
| サンプル7 | 構造式 (2) | $(CF_3SO_2)_3CLi$ | 0.5 | $3.64\times10^{-2}$ |
| サンプル8 | 構造式 (2) | $(CF_3SO_2)_3CLI$ | 1.0 | $3.80\times10^{-2}$ |
| サンプル9 | 構造式 (3) | $(CF_3SO_2)_2NLi$ | 0.5 | $4.62\times10^{-2}$ |
| サンプル10 | 構造式 (3) | $(CF_3SO_2)_2NLi$ | 1.0 | $4.80\times10^{-2}$ |
| サンプル11 | 構造式 (3) | $(CF_3SO_2)_3CLi$ | 0.5 | $2.75\times10^{-2}$ |
| サンプル12 | 構造式 (3) | $(CF_3SO_2)_3CLI$ | 1.0 | $2.88\times10^{-2}$ |

[0042] The result of Table 1 shows that each siloxane derivative shown by ** 6 --izing 8 has the conductivity which can be used for a cell. Moreover, in siloxane derivative (1) - (3) from which a coefficient of kinematic viscosity differs, it turns out that conductivity with higher using the siloxane derivative (1) which has a low coefficient of kinematic viscosity more can be obtained.
[0043] The cyclic voltamogram of the siloxane derivative (1) shown by ** 6 and ** 7 of the example 2 point and (2) was measured, and oxidation stability was investigated. Measurement used the electrochemical cell made from three electrodes, and used the lithium metal for the operation pole on the nickel electrode (diameter : 0.5mm), the counter electrode, and the reference pole. And potential until the oxidation current of 100microA-cm -2 occurs was made into the range of stable potential. Consequently, 5.8V and the oxidization stable potential of a sample 6 were set to 6.0V by the oxidization stable potential of a sample 2.
[0044] This result shows that a siloxane derivative can demonstrate the cell performance which was excellent also in the high voltage.
[0045] The coin cell siloxane derivative [ which is shown to LiCoO2 and a negative electrode by the carbon material, and is shown in the electrolytic solution by ** 6 ] (1) Used for example 3 positive electrode was produced, and the charge and discharge test was performed. Upper-limit voltage: Charge and discharge were repeated up to 20 cycles on condition that 4.2V, minimum voltage:3.0V, and discharge current:100microA. The charge and discharge test at that time is shown in drawing 1 .
[0046] The result of drawing 1 shows that a siloxane derivative (1) has the cell performance which was excellent as a cell.

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[Translation done.]

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## DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the property view showing the charge-and-discharge curve of the nonaqueous electrolyte cell of this example.

[Translation done.]

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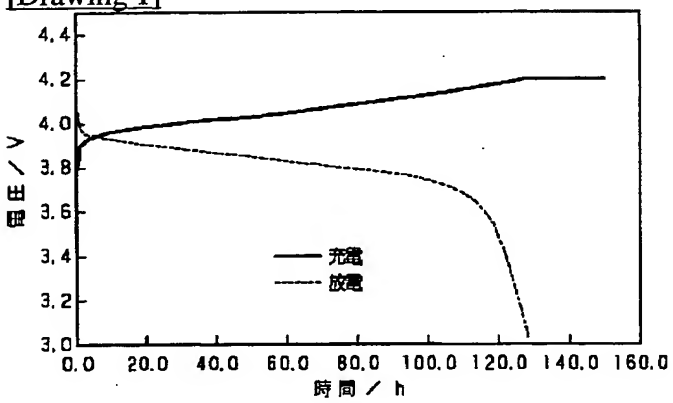
## DRAWINGS

[Drawing 1]




シロキサン電池の充放電曲線

[Translation done.]